

Phase Transition and NH₃ Motions in Polycrystalline [Ca(NH₃)₆](ClO₄)₂ Studied by Infrared Spectroscopy and Inelastic/Quasielastic Incoherent Neutron Scattering

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The examined compound [Ca(NH₃)₆](ClO₄)₂ was obtained from tetraaquacalcium chlorate(VII) according to the method proposed by Smith and Koch [1]. [Ca(NH₃)₆](ClO₄)₂ has two solid phases between 95 and 295 K: low-temperature phase (phase II) and high-temperature phase (phase I). The phase transition temperature at $T_C^h = 123.3$ K (on heating) and at $T_C^c = 122.0$ K (on cooling) was determined by means of differential scanning calorimetry (DSC), by extrapolating the T_{peak}^h and T_{peak}^c vs. rate of sample heating and cooling to the scanning rate value of 0 K·min⁻¹, respectively. The following thermodynamic parameters for phase I ↔ phase II transition were obtained: $\Delta H = 1.95 \pm 0.22$ kJ·mol⁻¹ and $\Delta S = 15.8 \pm 0.3$ J·mol⁻¹·K⁻¹. The large transition entropy indicates considerable configurational disordering in the high temperature phase (so called ODIC crystals). The thermal hysteresis of the phase transition temperature at T_c equal to ca. 1.3 K and the heat flow anomaly sharpness suggest that the detected phase transition is a first-order one. Room-temperature phase of this compound was analyzed by means of X-ray powder diffraction. Heksaamminecalcium chlorate (VII) crystallizes in the cubic system (Fm3m space group) with cell parameter: $a = 11.685$ Å and four molecules per unit cell. The crystal structure consist of octahedral [Ca(NH₃)₆]²⁺ cations and tetrahedral ClO₄⁻ anions. Therefore, the results of X-ray diffraction are very similar to those obtained earlier for [Ni(NH₃)₆](ClO₄)₂ and especially for [Mg(NH₃)₆](ClO₄)₂ [2,3]. Fourier transform middle infrared (FT-MIR) spectra were measured during cooling of the sample at temperatures ranging from 290 to 20 K. The appearing of two new bands in the wavenumber range of 3100 cm⁻¹ and 3200 cm⁻¹ at the vicinity of T_c , suggests that during phase transition crystal structure changes. The QENS and IINS spectra for [Ca(NH₃)₆](ClO₄)₂ were measured with NERA (Dubna in Russia) time of flight spectrometer at the following temperatures: 20, 110, 131 and 220 K. Neutron scattering elastic peak, registered at 110 K (low-temperature phase-II) and also at higher temperatures (high-temperature phase-I), shows distinct broadening, which is typical for dynamically, orientationally disordered crystals (ODIC). Fast reorientational motion of NH₃ ligands in [Ca(NH₃)₆]²⁺ can be pretty good described by a simple model of 120° instantaneous jumps around 3-fold axis on a picoseconds correlation time scale. The NH₃ ligands suddenly change neither the velocity nor the character of their reorientational motion at detected by DSC phase transition at T_c . The dynamical, orientational disorder is also confirmed by very much diffused spectra of the phonon density of states $G(\nu)$ for all temperatures higher than 20 K. It is due to great disorder connected with fast molecular motions, especially to the disorder of hydrogen atoms. Just the $G(\nu)$ spectra obtained for the low temperature phase at temperature 20 K show some peaks characteristic for ordered phase. Concluding the NH₃ groups perform fast stochastic reorientation below and above the phase transition.

[1] G.F. Smith, E.G. Koch, *Z. anorg. Chem.* 223 (1935) 17.

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[3] S. Hodorowicz, M. Ciechanowicz-Rutkowska, J.M. Janik, J.A. Janik, *Phys. Stat. Sol. (a)* 43 (1977) 53.